Photocatalytic Decomposition of Water Vapour on an NiO–$SrTiO_3$ Catalyst

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Summary The photodecomposition of water vapour proceeds steadily for more than 100 h on NiO–$SrTiO_3$ powder and stops immediately when the water vapour is removed.

SINCE the report of Fujishima and Honda[1] in 1971, many electrochemical studies have been carried out on the photocatalytic decomposition of water into hydrogen and oxygen, but few systems have been reported which decompose water vapour photocatalytically on solid surfaces.[2–4] Recently, Schrauzer *et al.*[2] have reported the photolysis of water using a TiO_2-based catalyst, but the catalytic activity decayed in a few hours.

We now report, for the first time, that $SrTiO_3$ carrying NiO on its surface catalyses the photochemical decomposition of water vapour and produces hydrogen and oxygen steadily. The reaction was performed in a conventional closed gas circulation system (350 ml), equipped with a quartz reaction vessel with a flat bottom (*ca.* 15 cm^2). An NiO(1·7 wt%)–$SrTiO_3$ catalyst (*ca.* 2g), which was prepared by the impregnation of $SrTiO_3$ powder (Ventron, 98·5% purity) with $Ni(NO_3)_2$ aqueous solution followed by calcination in air, was spread over the bottom of the reaction vessel. After evacuation of the system for 20 h at 450 °C, the catalyst was reduced by H_2 (*ca.* 100 Torr) at 300 °C for 20 h. This was followed by evacuation at 300 °C for 2 h and then reoxidation by O_2 at 300 °C for 3 h. After evacuation of the system at 300 °C for 2 h, water vapour (*ca.* 20 Torr) was introduced over the NiO (1·7 wt%)–$SrTiO_3$ catalyst in the reaction system at room temperature, and the catalyst was irradiated through the bottom by a 450 W, high-pressure, water-cooled, mercury lamp. The temperature of the vessel was 35 °C in the stationary state under the irradiation.

The evolution of H_2 ($4{\cdot}4 \times 10^{-3}$ ml/h) and O_2 ($2{\cdot}2 \times 10^{-3}$ ml/h) (ml measured at STP = standard temperature and pressure) was detected by gas chromatography (molecular sieve 5A column, Ar carrier) as shown in the Figure. When

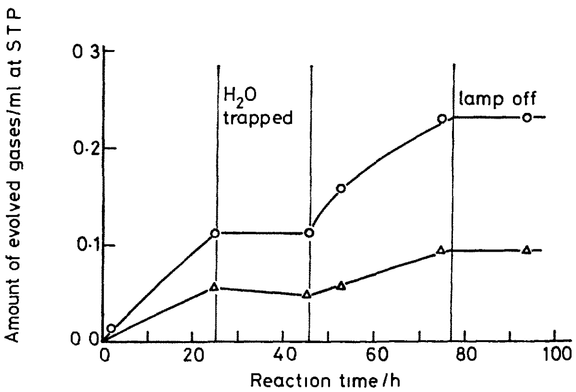

FIGURE. Photodecomposition of H_2O on NiO(1·7 wt%)–$SrTiO_3$. $p(H_2O)$ vapour = 20 Torr, 450 W high pressure mercury lamp. ——○——: Amount of evolved H_2(ml at STP); ——△——: amount of evolved O_2(ml at STP).

the water vapour was trapped by solid CO_2–methanol while the system was being illuminated, the evolution of H_2 and O_2 stopped at once; on releasing the trapped water again to the gas phase, the reaction continued. When the lamp was switched off, the evolution of H_2 and O_2 stopped immediately. The dependence of the rate of the H_2 evolution upon the pressure of water vapour was approximately first order in the lower H_2O pressure region (<10 Torr) and in the higher H_2O pressure region (>15 Torr) the activity was almost independent of the pressure. From these results, it was concluded that adsorbed water (which is in adsorption equilibrium with its vapour) is necessary for the continuous decomposition of water. On this catalyst the reverse reaction, to produce water from H_2 and O_2, did not proceed in the stationary state even when the water vapour was trapped, as shown in the Figure. For comparison, on Pt–$SrTiO_3$ we have also confirmed the evolution of H_2 under illumination, but when the water vapour was trapped, the amount of H_2 in the gas phase decreased continuously almost to zero, presumably owing to the synthesis of water. The evolution of O_2 depended markedly on the pretreatment conditions.

We found that the decomposition of water vapour under illumination did not proceed on $SrTiO_3$ or on NiO alone under similar conditions and that the contact of $SrTiO_3$ with NiO is necessary for the photocatalytic decomposition of water. This decomposition also proceeded on a cobalt oxide–$SrTiO_3$ system. It is notable that when these catalysts were suspended in the water, the decomposition activity increased considerably.

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